Gold-catalysed synthesis of polypyrrole

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1 Introduction

Since the first preparation of the highly conducting polyacetylene (PA) in 1977, much effort has been devoted to the synthesis of other organic conducting polymers such as polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh) and their applications in devices combining optical, electrochemical and conducting properties. Among these innovative materials, PPy is appealing because of its tuneable conductivity and stability in air [1] that allow applications in electronic displays, [2] electrode materials, [3] molecular electronic circuit elements, [4] restoration of data, [5] indicators of gasometers [6] and biochemical analysis [7].

Considering the physico-chemical correlations, the electrical conductivity of PPy is attributed to the electrons hopping along and across the polymer chains with conjugating bonds [8,9]. In particular, the more positively charged PPy, the more available electron holes, the longer polymer chains and the more coplanarity between interchains are favourable conditions for a higher conductivity performance [10].

Conducting polypyrrole can be prepared by chemical, [11] electrochemical, [12] plasma, [13,14] vapour phase [14,15] and enzymatic routes [17].

Considering the conventional chemical syntheses, they involve stoichiometric amounts of oxidants as Fe^{3+}, Ag^+, I_2, Br_2 [18] with consequent environmental problems related to the disposal of the by-products. On the other hand, the enzymatic route based on the metal-enzyme *Laccase* is attractive but still remains a method for small scale preparation. More interestingly, the electrochemical preparation of polypyrrole has been explored in recent years as a tool for film deposition [19]. Chemical oxidation routes have been reconsidered making use of more environmentally friendly reagents as air, O_2 and H_2O_2. In this context, an early work of Dias *et al.* investigated the preparation of polypyrrole using hydrogen peroxide as the oxidant in the presence of catalytic iron(III) [18]. Toshima et al. reported the polymerization of pyrrole using molecular oxygen in the presence of a rather complex catalytic system, $AlCl_3$-CuCl, producing a polymeric material contaminated by organic chlorine, carbonyl and hydroxyl derivates having a negative effect on the electronic conductivity [20]. The use of a soluble iron (III) catalyst in connection with a water-organic solvent medium resulted in an improved synthesis [21].

Successful use of conventional oxidation catalyst, as supported platinum group metals, using O_2 and H_2O_2 is presently unknown probably owing to the poisoning effect of the heterocyclic nitrogen on the noble metals [22].

Recently, metallic gold has been proved to be an efficient catalyst in both homogeneous and heterogeneous oxidation [23,24,25]. Supported gold showed high efficiency in the oxidation of alcohols, polyols, aldehydes [26-30]. Among the typical properties of gold catalysis, some of them should be outlined: the first is that only nanometric particles either in form of conventional supported catalyst or as "naked"

colloidal nanoparticles, show catalytic activity [30], and the second one is related to the compatibility of gold with nitrogen-containing compounds, as amines [31]. Moreover, in some applications, beside O_2, also H_2O_2 can be used as the oxidant [32].

Owing to these outstanding properties and the present interest in the synthesis of conductive polymers, we have investigated the oxidative polymerization of pyrrole using O_2 and H_2O_2 as the oxidants in aqueous solution under mild conditions in the presence of colloidal gold catalyst.

2 Experimental

2.1 Reagents
Pyrrole (98%), H_2O_2 (30%), HCl (standard solution 1 M), gold sponge (99.999%), D(+)-glucose monohydrate (≥99%), sodium borohydride powder (98%), KBr (≥99.0%),1-methyl-2-pyrrolidone (≥98%) and acetone 99% were from Fluka and gaseous oxygen (99.99%) and air from SIAD.

2.2 Colloidal dispersion of gold
As previously reported, [30] a colloidal dispersion of gold was prepared by treating a 2.5 x10^{-4} M aqueous solution of gold (as HAuCl$_4$) with NaBH$_4$ (NaBH$_4$:Au=5:1 w/w) under N$_2$ atmosphere, in the presence of a large excess of glucose as a stabilizer (0.35 M). The resultant brown sol contained metal particles, stable for several hours, having a mean diameter of 3.6 nm, as determined by TEM and Scherrer XRD analysis. A less stable dispersion, prepared in the absence of glucose, was also used for comparison in exp. 4', Table 1, for excluding any interference of glucose.

Table 1

Aerobic polymerization of pyrrole with air. Reaction time 3 days

Experiment	Py/Au (molar ratio)	Yield%
1	No gold	0
2	10000	42
3	5000	50
4	1000	75
4'	1000	73

2.3 Aerobic polymerization of pyrrole
a) In a 100 ml glass reactor equimolecular quantities of pyrrole (Py) and HCl (15 mmol) were dissolved in water (30 mL) and magnetically stirred in air at 0.3MPa for 3 days at room temperature (292-295 K) in the absence and in the presence of different amounts of colloidal gold quantified in the tables by the Au/Py molar ratio. The gaseous atmosphere was discharged and replaced

with fresh air every 2 hours. At the end of the test, the dark insoluble material was collected by filtration. The yield, shown in table 1, was evaluated after washing the product with water and acetone, and drying at 383 K overnight.

b) Similar experiments were carried out using pure dioxygen instead of air, at 0.3MPa, and small samples were withdrawn for analysis during the test. The related results are reported in table 2.

Table 2

Catalytic polymerization of pyrrole with O_2 at 0.3 MPa and different reaction times

Experiment	t (h)	Py/Au (molar ratio)	Yield%
5	8	No gold	0
6	"	10000	0
7	"	1000	1
Experiment	t (h)	Py/Au (molar ratio)	Yield%
8	16	No gold	5
9	"	10000	31
10	"	1000	34
Experiment	t (h)	Py/Au (molar ratio)	Yield%
11	24	No gold	10
12	"	10000	50
13	"	5000	60
14	"	1000	82
Experiment	t (h)	Py/Au (molar ratio)	Yield%
15	72	No gold	12
16	"	10000	61
17	"	5000	72
18	"	1000	99

2.4 Polymerization of pyrrole using H_2O_2 as the oxidant
Pyrrole (15 mmol) and HCl 1M (15 mmol) were dissolved under nitrogen atmosphere in water (30mL) and the reported amounts of colloidal gold were added. To this mixture, H_2O_2 (15 mmol) was added drop by drop during 10 min. Stirring was prolonged at room temperature for 24 h. The dark precipitate was filtered, washed with water and acetone, and dried at 383 K overnight. The resulting yields are reported in table 3.

2.5 Ac-Impedance spectroscopic measurements
Electrical properties of polymers were determined with a standard conductivity cell (CON-H Material Mates, Fig. 3) provided with two compartments within the electrical contact is assured by flat and circular (S=1.15 cm^2) plates of platinum.

Table 3

Catalytic polymerization of pyrrole using H_2O_2 as the oxidant. Reaction time 24 h

Experiment	Py/Au (molar ratio)	Yield%
19	No gold	57
20	10000	66
21	5000	90
22	1000	99

The specific electrical conductivity σ (S cm^{-1}) of the pellets was obtained by measuring the bulk pellet resistances R (Ω) through Electrochemical Impedance Spectroscopy (EIS). AC-Impedance tests were performed on pressed pellet of polymers using an AUTOLAB PGSTAT 30 Metrohm in the frequency range from 10 mHz to 1 MHz with applied excitation ac-voltage of 10 mV rms. This instrument uses a four-point system suitable for measuring the resistance or conductivity of samples excluding the contact resistance. All impedance measurements were taken under 0 V, 0.5 V and 1 V at room temperature and static air. Pellets for conductivity examination were prepared by uniaxial press of the powder into a 16mm diameter die at 200 MPa for 30 min. This procedure was selected because it ensures a suitable statistical distribution of the chains. The thickness of the pellets were measured with an analogical spessimeter ensuring an accuracy of 0.01 mm

2.6 TEM, IR and XRD measurements

The morphological characterisation of the polypyrrole materials was performed by transmission electron microscopy (TEM; LEO 912AB microscope). The TEM determinations were done by deposing a drop of the solid ultrasonically dispersed in water onto a carbon–coated copper grid (FCF 200 mesh) and allowing them to dry in oven at 60°C for several hours. FT-IR spectra were recorded as KBr dispersions by a JASCO FT-IR-410 instrument in the 380-4000 cm^{-1} range.

XRD spectra were recorded using a Rigaku D III-MAX horizontal-scan powder diffractometer with Cu Kα radiation.

3 Results and discussion

3.1 Oxidative polymerisation of pyrrole

When the aqueous 0.15 M solution of pyrrole hydrochloride was stirred at room temperature for three days under air at 0.3 MPa in the absence of catalysis, no insoluble product was collected from the dark solution, meaning that only low molecular weight polymers were formed. On the contrary, by adding colloidal gold to the reactants, a dark polymeric material, insoluble in acetone, was formed whose yield increased by increasing the gold concentration up to 75% (table 1). In all the experiments, the gold amount was less than 0.1% with respect to the reacting monomer.

Using pure oxygen gas, a slow auto-oxidation produced a modest yield of insoluble polymer (12%) after 3 days. On adding colloidal gold, a strong catalytic effect was detected (table 2): the polymeric material was formed with almost total yield (99%) after 3 days.

Using hydrogen peroxide as the oxidant, a consistent polymerization of pyrrole was observed also in the absence of catalyst. In fact, as shown in table 3, the reaction occurred with 57% yield with respect to pyrrole in 24 h. However, also in this case, a catalytic contribute of gold was demonstrated
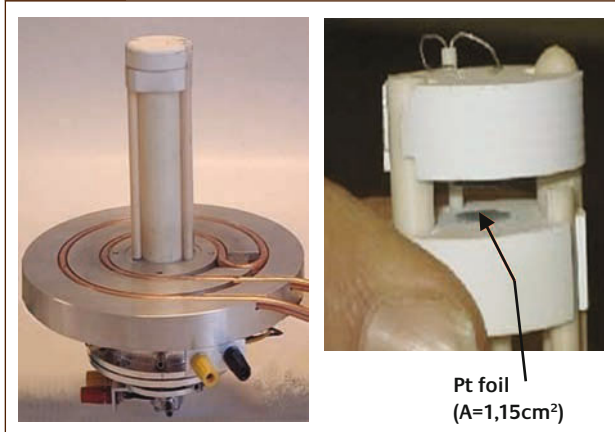
Figure 1
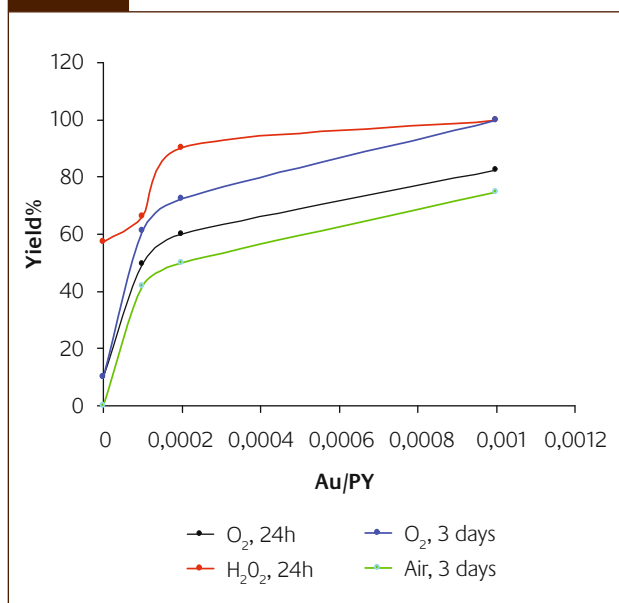
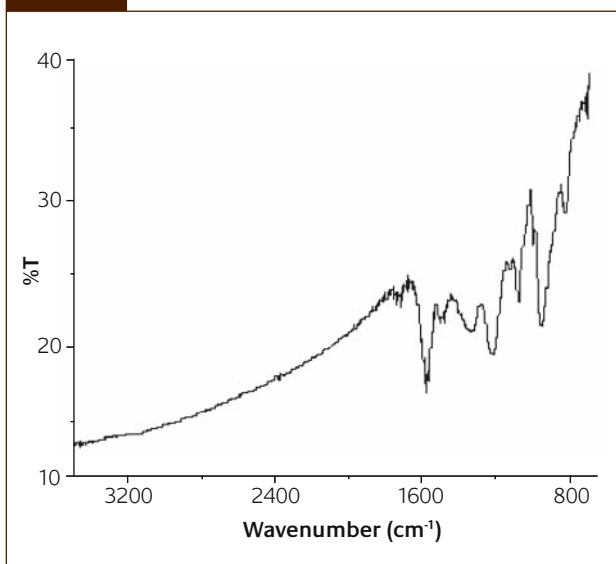*Gold effect in the polymerization of pyrrole by air, O_2 and H_2O_2*

Figure 2
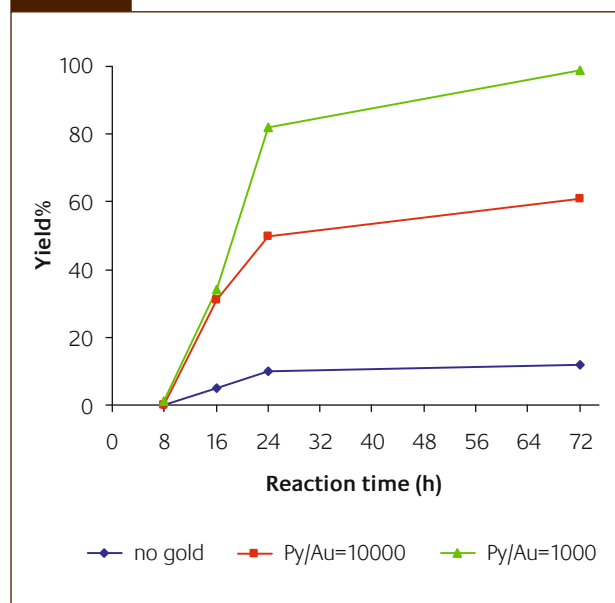
Kinetic data of pyrrole polymerization under O_2

Figure 3

Pt foil
(A=1,15cm²)

Test station (CON-H Materials Mates) for conductivity measurements

Figure 4

FT-IR spectrum of a PPy sample in KBr

because the yield increased up to 99% by adding a small quantity of colloidal metal (Py/Au=1000, table 3).

The catalytic effect of gold in PPy formation with different reagents is summarized in Fig. 1.

The kinetics of polymeric material formation was followed during pyrrole polymerisation by dioxygen in the presence of different quantities of gold, as illustrated in Fig. 2. Independently from the amount of catalyst, the reaction produced a detectable solid material only after 8 h; during this time oligomeric products have been formed, as indicated by the dark colour assumed by the reacting solution. After the induction time, the rate of PPy formation increased with the amount of catalyst.

Figure 5
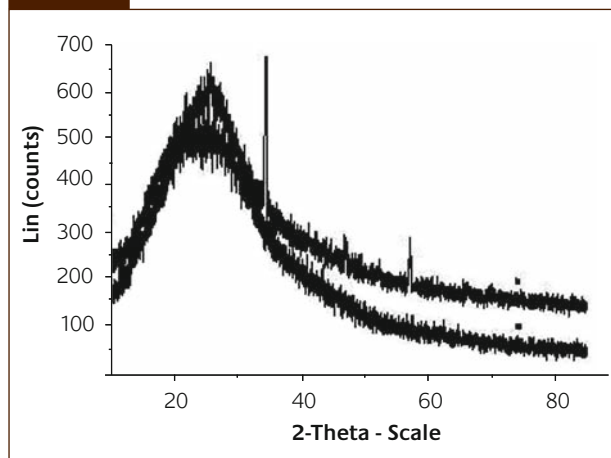
X-ray diffraction patterns of PPy synthesized in the absence (a) and in the presence (b) of gold nanoparticles

3.2 Structural analysis of the products by IR and XRD techniques

According to the literature, IR spectroscopy is one of the most conventional and powerful techniques for analyzing the structure of polypyrrole. [34] Independently from the synthetic method, all the prepared polymers show a similar IR spectrum which is represented in Fig. 4. As expected for conductive polymers, a broad pattern in the range 4000-2000 cm⁻¹ was observed which is due to the presence of the conjugated electron system producing the so called "tail of the electronic absorption band".[19]

The peaks at 1560 and 1471 cm⁻¹ can be assigned to C=C stretching vibration and the shoulder at 1385 cm⁻¹ along with the band at 1311 cm⁻¹ to N-C group (stretching vibration and deformation vibration respectively). Also the characteristic bipolaron bands at 1196 and 923 cm⁻¹ confirm the formation of PPy.[35] The absence of a strong absorption around 1700 cm⁻¹ and at 1600 cm⁻¹ indicates the absence of undesired carbonyl groups.[36]

Fig. 5a shows typical X-ray diffraction patterns of PPy synthesized in the presence and in the absence of gold nanoparticles. The broad peak around $2\theta = 21°$ is associated with the closest distance of approach of the planar aromatic rings of pyrrole.[37] The XRD pattern in Fig. 5b shows, beside the polypyrrole peak, reflections at $2\theta \approx 38°$, $48°$, $63°$ and $78°$ due to the presence of Au particles. Although the presence of gold is not clearly evidenced by TEM images, the XRD pattern of the polymeric material (Fig. 5 b) showed the typical reflections of metallic gold particles having a calculated mean diameter of 42 nm. Therefore, an important agglomeration of the 3.6 nm gold particles took place during the polymerisation reaction.

Figure 6

A) By H$_2$O$_2$, no Au

B) By H$_2$O$_2$, Py/Au=1000

C) By air, no Au

D) By O$_2$, no Au

E) By O$_2$, Py/Au=5000
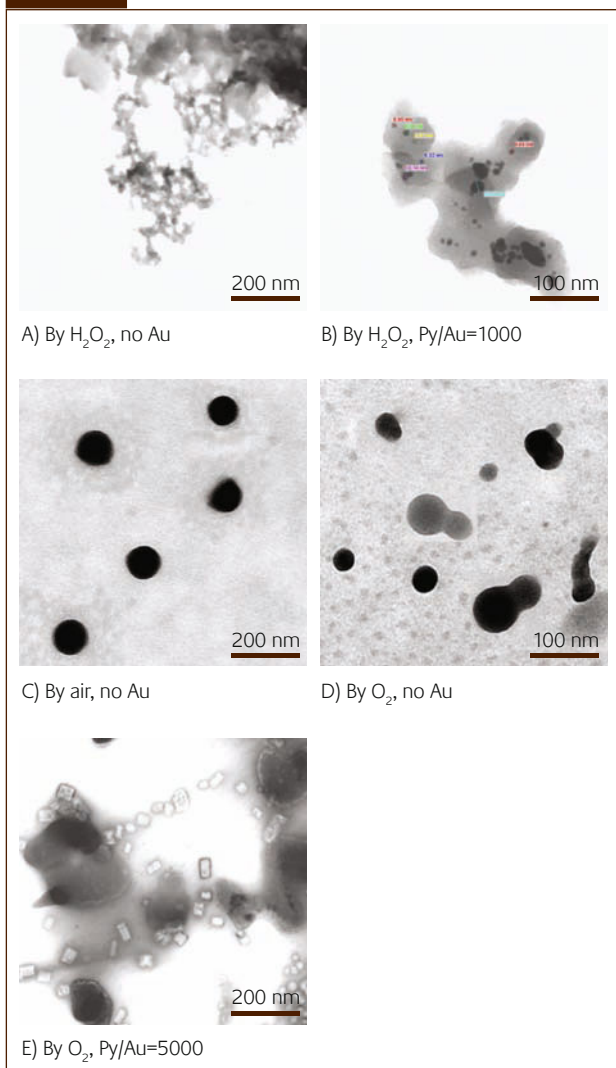
*TEM images of different polypyrrole samples*

3.3 Polymer morphology by transmission electron microscopy (TEM)

The TEM images of various polymeric materials obtained in the present study are reported in figures 6 A-E. Comparing different products, the morphology is mainly influenced by the nature of the oxidising reagent. By using H$_2$O$_2$, the quick polymerization led to a partly reticulated structure in the absence of gold (Fig. 6A) and to amorphous material using gold catalysis (Fig.6B).

The low yield, non-catalyzed polymerization with gaseous oxygen produced more ordered structures represented by 40-80 nm spheres (Fig.6C, 6D), whereas a large amount of curious thin squares (20-60 nm) were observed in the high yield polymerization catalysed by gold (Fig. 6E). This latter structure is unusual also in the context of conventional polymerizations of pyrrole and could be of interest for tailor-made composite applications.

The low percentage of gold catalyst does not allow a precise TEM identification of the metal in the final product:

Figure 7
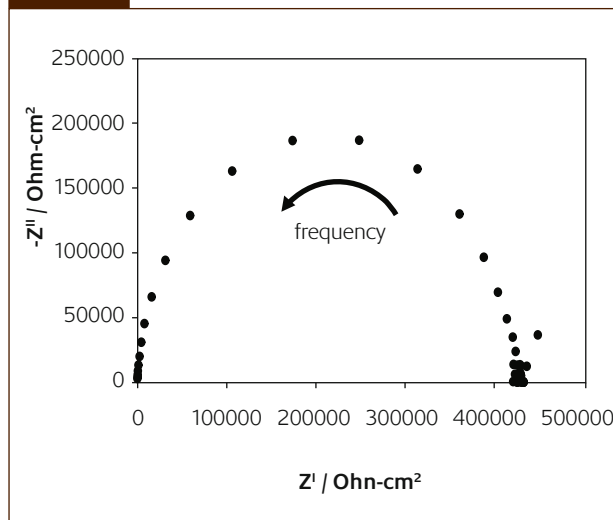
Nyquist plot of a polypyrrole sample at 0V

However, the technique is sometimes diagnostic as shown by fig. 5A (no gold) and 5B (gold present). In any case, the physico-chemical behaviour of the polymer should be not affected by such a low amount of metal, in contrast with the heavy influence of gold when used by Mallick as a stoichiometric oxidant in aniline polymerization. [38-40]

3.4 Ac-Impedance spectroscopic studies

Fig. 7 shows a typical Nyquist plot of AC-Impedance measurements. The spectrum is a plot of imaginary part (Z") vs real part (Z') of the impedance measured as a function of frequency ω which increases from right to left.

The intercepts of the semicircle with the real axis are correlated to the physical resistances. The intercept at high frequency is due to the bulk resistance (R$_s$) whereas the intercept at low frequency is correlated to slow processes (e.g. diffusion processes).

In the high frequency region of the spectra, all polymers showed a similar behaviour. At low frequency, the polymers obtained in the experiments 19 and 22 exhibited a typical RC nature (resistor-capacitor circuit) whereas the samples of experiments 3,18 and 21 revealed an additional Warburg element (semi-infinite diffusion).[41] The materials obtained in the experiments 2, 4 and 20 produced a noisy signal at low frequency. The last case is a well known behaviour due to charge transfer phenomena [42] which does not compromise the evaluation of the bulk resistance (R$_s$).

The conductivity correlated to the bulk resistance of the synthesized polypyrrole materials is similar to that obtained in conventional chemical polymerization using stoichiometric reagents.

The σ values, determined for various preparations and measured in samples of different thickness under different voltages (table 4), ranged from $2.7.10^{-4}$ to 5.10^{-3} S·cm^{-1}, which are typical for polymers obtained by using FeCl$_3$, AgNO$_3$,

Cu(NO$_3$)$_2$-AlCl$_3$,[43] VO(acac)$_2$-AlCl$_3$-O$_2$, [44] AlCl$_3$-CuCl-O$_2$ [20] but much lower than the values generally found in electrochemical polypyrrole film deposition. [19] A synthetic comparison of σ values is reported in table 5.

It should be pointed out that the effect of pressure, pressing time and interval between pressing and testing, which can modify the interchain and intrachain conductivity of the polymers, were not evaluated.[33]

Table 4

Conductivity data of polypyrrole samples

Sample (thickness [mm])	0V (S·cm^{-1})	0.5V (S·cm^{-1})	1V (S·cm^{-1})
2 (0.69)	2.46·10^{-3}	5.88·10^{-4}	4.80·10^{-4}
3 (1.10)	5.09·10^{-3}	1.38·10^{-3}	3.84·10^{-3}
4 (0.63)	8.94·10^{-4}	1.39·10^{-3}	4.09·10^{-3}
18 (0.64)	8.47·10^{-4}	9.97·10^{-4}	7.23·10^{-4}
19 (0.60)	1.33·10^{-3}	6.17·10^{-4}	3.34·10^{-4}
20 (0.67)	4.81·10^{-3}	2.70·10^{-3}	4.85·10^{-3}
21 (0.64)	9.00·10^{-4}	6.04·10^{-4}	4.56·10^{-4}
22 (0.68)	2.74·10^{-4}	5.53·10^{-4}	4.97·10^{-4}

Table 5

Comparison of conductivity data

Results	Conductivity (S·cm^{-1})
Ours	2.7·10^{-4}-5.1·10^{-3}
Chao and March [40]	5.0·10^{-3}-2.8
Toshima and Tayanagis [20]	10^{-2}
Izumi and Toshima [41]	10^{-10}-2.1·10^{-2}
Diaz and Fanazawa [19]	10-100

4   Conclusions

A new catalytic method for the clean aerobic polymerization of pyrrole, by using gold as a catalyst under environmentally friendly conditions, has been investigated. Nanometric gold particles resulted very active when used in a limited amount of gold (1:1000 molar ratio and less) allowing the total polymerization of the monomer at room temperature under a moderate pressure of dioxygen. The conducting polymer obtained by this method is of high quality being free from carbonyl groups. The TEM images show different morphologies ranging from amorphous material to well shaped materials, as spheres and squares, depending on the nature of the oxidizing reagent. Some particular features, as thin squares of PPy have been formed only by catalytic assistance of gold.

Ac-impedance spectroscopic measurements show low conductivities probably due to distortion in the polymer chains which commonly occurs also in stoichiometric chemical oxidation of pyrrole.

About the authors
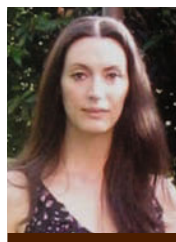
Cristina Della Pina received the master degree at Milan University and awarded the Ph.D. degree in Industrial Chemistry in 2006. Her work focuses on the development of heterogeneous catalysts.

Ermelinda Falletta got her master degree in Organic Chemistry at the University of Palermo. In 2005 she joined Prof. Rossi's research group at Milano University involved in catalytic oxidation of organic compounds.

Massimiliano Lo Faro graduated in Industrial Chemistry in 2002, and earned the PhD in Material Sciences at the University of Rome in 2008. Since 2003 he is working at the Institute of Advanced Technology for Energy (CNR-ITAE "Nicola Giordano") in the field of Fuel Cells chemistry.

Mauro Pasta earned his master degree in Industrial Chemistry at University of Milan in 2007. He is working on his PhD thesis concerning gold catalysis applied to chemical and electrochemical oxidation carbohydrates.

Michele Rossi obtained his master degree in Industrial Chemistry at the University of Milan where presently he is full professor of Chemistry. His research was mainly devoted to the activation of small molecules and was a pioneer in the application of gold catalysis to the liquid phase oxidation of alcohols and sugars.

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